SPECTROSCOPIC OBSERVATION OF WATER-MEDIATED DEFORMATION OF THE CARBOXYLATE-M^{2+} (M= Mg, Ca) CONTACT ION PAIR

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The binding of alkaline earth dications to the biologically relevant carboxylate ligand has previously been studied using vibrational sum frequency generation (VSFG) spectroscopy of the air-water interface, infrared multiple photon dissociation (IRMPD) spectroscopy of clusters, and DFT methods. These results suggest the presence of both monodentate and bidentate binding motifs of the M^{2+} ions to the cayboxyl head groups depending on the extent of solvation. We revisit these systems using vibrational predissociation spectroscopy to measure the gas-phase vibrational spectra of the D_2-tagged microhydrated $[MgOAc(H_2O)_{n=1-5}]^+$ and $[CaOAc(H_2O)_{n=1-6}]^+$ clusters. The spectra show that $[MgOAc(H_2O)_n]^+$ switches from bidentate to monodentate binding promptly at n = 5, while $[CaOAc(H_2O)_n]^+$ retains its bidentate attachment such that the sixth water molecule initiates the second solvation shell. The difference in binding behavior between these two divalent metal ions is analyzed in the context of the local acidity of the solvent water molecules and the strength of the metal-carboxylate and metal-water interactions. This cluster study provides insight into the chemical physics underlying the unique and surprising impacts of Mg^{2+} and Ca^{2+} on the chemistry mediated by sea spray aerosols. Funding for this work was provided by the NSF's Center for Aerosol Impacts on Climate and the Environment.